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LUBRICITY PROPERTIES OF HIGH TEMPERATURE JET FUEL

By: L. Grabel

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The effects of fuel additives and naturally occurring fuel components and impurities on the lubricity of JP-5 were determined. The ball-on-cylinder machine was used as a lubricity tester. Naturally occurring hydrocarbon compounds had very little effect on the lubricity of JP-5. Corrosion inhibitors, organic acids and nitrogen containing compounds were found to improve lubricity while sulfur compounds, non-acid oxygen containing compounds and anti-oxidants had little or no effect on lubricity. The

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compounds that were effective lubricity improvers did so by keeping dissolved oxygen from reaching the metal surface of the ball-on-cylinder machine and reacting there.

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PROPULSION TECHNOLOGY AND PROJECT ENGINEERING DEPARTMENT

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LUBRICITY PROPERTIES OF HIGH TEMPERATURE JET FUEL

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CONVERSION FACTORS: SI TO U.S. CUSTOMARY UNITS

Convert From	TO	Multiply by
inch	metre	2.54×10^{-2}
pounds/1000 barrels	Kilograms /metre^3	2.85×10^{-3}
degrees Fahrenheit	degrees Celsius	$t_C^o = \frac{(t_F^o - 32)}{1.8}$

INTRODUCTION

The sudden failure or malfunction of fuel lubricated aircraft components such as fuel pumps and fuel controls can have disastrous consequences. The probability of lubricity related malfunctions has increased with the introduction of more sophisticated engines and the use of more severely hydrotreated fuel necessitated by the energy crisis. The Navy recently experienced lubricity problems involving a hang-up in the fuel control of the TF30-P-408 engine in the A-7B aircraft. In order to alleviate this problem, the Navy has been adding Hitec E-515, an approved corrosion inhibitor that is known to improve lubricity, to fuel onboard aircraft carriers on which A-7B/C's are deployed.

In order to more fully understand the causes of lubricity problems and to have a means of solving them if they do occur, the Navy initiated a program to determine the factors that affect fuel lubricity and to develop a way of maintaining good lubricity. This work was begun in FY 1975 and continued through FY 1977. The authorization for FY 1977 is listed in reference 1.

The test instrument used in the program is the Ball-on-Cylinder Machine (BOCM), a device that reports had shown was capable of distinguishing between good and poor lubricity fuels as well as being able to detect the known beneficial effects of corrosion inhibitors on poor lubricity fuel.

In addition to its own work, the Navy is also cooperating with the Coordinating Research Council Aviation Fuel Lubricity Group in evaluating the repeatability and reproducibility of the BOCM.

CONCLUSIONS

1. The BOCM can be used to distinguish between fuels with good and poor lubricity.

2. The primary factor affecting the lubricity of jet fuels is the type and amount of non-hydrocarbon impurities in the fuel. Hydrotreating and clay filtration remove impurities from the fuel and thus make its lubricity worse.

3. Changes in fuel composition within specification limits do not significantly affect the lubricity of JP-5.

4. Organic acids and most types of nitrogen containing impurities improve the lubricity of JP-5, while sulfur compounds and non-acid oxygen containing impurities either have no effect or a slight detrimental effect on lubricity.

5. Corrosion inhibitors improve the lubricity of JP-5. Their effectiveness increases with increasing concentration in their allowable concentration range.

6. Anti-oxidants and anti-icing additive have no effect on lubricity in their allowable concentration range.

7. The addition of 10-20 percent of a fuel with good lubricity to one with poor lubricity will usually result in a fuel with acceptable lubricity.

8. Deoxygenation significantly improves the lubricity of fuels with poor lubricity; however, it has little or no effect on fuels that already have good lubricity.

9. Most current JP-5 fuels contain a sufficient amount of naturally occurring non-hydrocarbon impurities to provide good lubricity.

RECOMMENDATIONS

1. The BOCM should continue to be used to evaluate fuels suspected of causing problems because of poor lubricity and to monitor fuel samples from the fleet to prevent future lubricity problems.

2. Whenever possible, hydrotreated fuels should be mixed with non-hydrotreated fuels before use to prevent problems due to poor lubricity.

3. Corrosion inhibitors should be added to fuels to improve their lubricity when necessary.

4. The Navy should continue to cooperate with the Coordinating Research Council-Aviation Fuel Lubricity Group in evaluating the repeatability and reproducibility of the BOCM.

DESCRIPTION

1. The BOCM is a device for measuring the effects of various fluids on wear and friction. A schematic of the device is shown in figure 1 and a photograph of the basic instrument is shown in figure 2. Figure 1 should be referred to in conjunction with the description that follows. Letters in parentheses refer to specific items in figure 1.

2. The BOCM consists of a non-rotating 0.5 inch diameter steel ball (A) held in a vertically mounted chuck (B) and forced against the highest point on the outer surface of a 1.75 inch diameter steel cylinder (C). Detailed specifications for the ball and cylinder are found in Appendix A. The ball and cylinder are positioned inside an open topped rectangular reservoir (D) that contains a sufficient amount of test fluid to cover the bottom portion of the cylinder. The cylinder is axially mounted on a horizontal shaft (E) that passes through the sides of the reservoir and is connected to a variable speed motor (not shown). The entire apparatus is mounted on a phenolic base (F).

3. Holes drilled in the base and side of the reservoir (G) allow purge gas of a desired composition and humidity to be bubbled over and through

the test fluid. The humidity of the purge gas is controlled by volumetrically mixing dry gas (passed through "Drierite" (W. A. Hammond Company brand of calcium sulfate)) and saturated gas (bubbled through two water filled spargers in series) in the desired proportions.

4. There is no system for controlling the temperature of the test fluid in the BOCM; initial fluid temperature is determined by ambient conditions. A thermocouple (not shown) located on the bottom of the reservoir is used to record the temperature of the test fluid.

5. Load is applied to the cylinder by hanging weights on the hook (H) at the end of the balance beam (J). The balance beam is designed so that the ball is located exactly midway between the pivot point (K) and the weight hook (H). This makes the vertical load on the ball equal to twice the load applied at the weight hook.

6. The BOCM can also be set up to measure the frictional force between the ball and cylinder. Other operators, however, found that wear measurements were much more sensitive to differences between fuels than friction measurements. This was confirmed during early experiments with the BOCM and all remaining tests were performed using wear as the only measurement of lubricity.

METHOD OF TEST

1. Standard Operating Conditions for BOCM. Work done by other BOCM operators prior to the Naval Air Propulsion Test Center's (NAPTC's) acquisition of its instrument resulted in the establishment of a set of standard operating conditions for the BOCM. These conditions are as follows:

a. Load: 1000 g

b. Speed: 240 rpm

c. Duration: 32 minutes

d. Fuel Volume: 25 ml

e. Test Fluid Temperature: 77 $\pm$ 3°F (25 $\pm$ 1.5°C) at beginning of test.

f. Purge Air: 10 percent Relative Humidity, 77 $\pm$ 3°F (25 $\pm$ 1.5°C) temperature.

g. Purge Air Flow Rate: 10 standard cubic feet per hour bubbling over and through test fluid.

h. Pretreatment of Fuel in Reservoir: 15 minutes

Unless otherwise noted, all results included in this report were obtained under these conditions.

2. Operating Procedure.

a. The ball, cylinder and inside of the reservoir are all cleaned

with solvent and dried by suction to remove any outside contaminants or residue from previous runs. Details of the cleaning procedure are found in Appendix B. The position of the cylinder is adjusted so that the ball is in contact with fresh surface. The test fluid is added to the reservoir and sparged with gas of the desired composition and humidity for 15 minutes. The motor is then turned on and the cylinder brought to operating speed of 240 rpm. The rotation of the cylinder carries test fluid into the ball-cylinder contact area. The desired amount of weight is then hung from the weight book and the timer started. The test is continued for 32 minutes. Removable teflon covers are used on top of the reservoir to prevent contamination and to make it easier to maintain a constant humidity and gas composition inside the reservoir. The purge gas is left on throughout the test. At the end of the test, the weight is removed, the motor shut off and the ball removed from the chuck.

b. The rotation of the cylinder against the ball produces a wear scar on the ball and a wear track on the cylinder. The size of the wear scar is a measure of the lubricity of the test fluid; the larger the scar, the poorer the lubricity.

DISCUSSION AND ANALYSIS OF RESULTS

1. Repeatability of Results.

a. The quality of test results depends to a large extent on how accurately they can be repeated. Random variations in operating parameters can cause unwanted variability in BOCM results. The extent of this variability and the effects of several operating parameters on it are discussed in following paragraphs.

b. Day to day variability. The day to day variation in WSD of three JP-5 fuels run under standard operating conditions was measured. The first fuel had an average WSD of 0.34 mm with a standard deviation of 0.019 mm (9 runs). The second fuel had an average WSD of 0.41 mm with a standard deviation of 0.031 mm (13 runs). The third fuel had an average WSD of 0.63 mm with a standard deviation of 0.047 mm (9 runs). The increase in standard deviation with increasing WSD agrees with the data of Garabrant (reference 2), who found that the absolute size of the test error increased with increasing WSD whether the increase was caused by changes in fuel properties or operating conditions.

c. Causes of variability. There are a number of factors that can effect WSD's. They include cylinder hardness and surface finish, ball hardness and surface finish, test duration, load, rpm, inlet air temperature and humidity, and cylinder cleanliness. Those variables that could be adjusted independently were studied to see if any of them were the possible cause of a significant amount of random error. Test results are summarized below.

(1) Test duration, load and RPM. The effect of small changes in test duration, load and RPM on WSD is shown in Table I. The data indicates

that random variations in these parameters, which are expected to be considerably smaller than the variations shown in Table I, will not significantly effect test results.

(2) Inlet air temperature and humidity. An estimate was made of the effects that random variations in inlet air temperature and humidity could have on WSD. Calculations were based on lab data showing that, in the range of 5-20 percent R.H. inlet air, WSD of a typical JP-5 fuel increases by approximately 0.01 mm for every two percent increase in relative humidity. The maximum random variation in inlet air temperature about the standard 77°F operating temperature was estimated to be ±3°F. The maximum random variation in inlet air humidity about the standard ten percent R.H. was estimated to be ±3 percent R.H. Results showed that the maximum error in WSD due to random variations in inlet air temperature and relative humidity (equivalent to going from 77°F, ten percent R.H. to either 74°F, seven percent R.H. or 80°F, 13 percent R.H.) would be about 0.02 mm. The average error due to temperature and humidity variations should be considerably smaller. The effect of large changes in inlet air humidity is presented in paragraph 11.

(3) The effects of the other variables listed in paragraph 1.c. could not be individually estimated.

2. Definition of "Real" Changes in WSD.

a. In the process of evaluating the effects of various compounds on lubricity, it became necessary to decide when the difference between two measured WSD's was "real" and when it could be attributed to random variations. It was decided that if the difference between two measured WSD's was greater than two standard deviations it would be considered "real"; if not, it would be attributed to random variations. On the basis of the data in paragraph 1.b. and the fact that most of the clay filtered JP-5 fuels used as base fluids had WSD's between 0.55 and 0.60 mm under standard conditions, two standard deviations were determined to be ±0.09 mm.

b. In cases where fuels other than clay filtered JP-5 were used as base fuels, the criterion for determining real changes was adjusted according to the initial WSD of the fuel.

3. Definition of Good and Poor Lubricity Fuels.

a. The only way of establishing a definition of a poor lubricity fuel is to obtain samples of fuels that are known to have caused problems in the field because of poor lubricity and measuring their WSD's. Reference 3 reported that two JP-4 fuels that caused problems gave WSD's of 0.58 and 0.51 mm under standard operating conditions. Reference 4 reported that a JP-5 fuel known to have caused lubricity problems gave a WSD of 0.49 mm under standard conditions.

b. A survey of fuels with good lubricity (no reported field problems) revealed that none of them produced a WSD larger than 0.42 mm under standard conditions.

c. Thus, a poor lubricity fuel can be defined as one which produces a WSD of 0.49 mm or greater under standard operating conditions. A good lubricity fuel can be defined as one which produces a WSD of 0.42 mm or less under standard conditions. Fuels giving WSD's between 0.43 and 0.48 mm under standard conditions are considered marginal and their acceptability would depend on the severity of operating conditions.

4. Base Fuel.

a. This project is concerned with determining the factors that affect the lubricity of JP-5. There are two ways of approaching the problem. One is to evaluate different variables using a pure compound or combination of compounds as a base fuel. This is advantageous because it limits the number of components in the system, is easily analyzed and can be reproduced at other laboratories. The main drawback to using pure compounds is finding a system that will react the same way as JP-5. The second method is to evaluate different variables using JP-5 as a base fuel.

b. In surveying the literature to find a suitable compound for use as a base fuel it was found that certain combinations of materials give unexpected results; for example, mixing low concentrations of a polycyclic aromatic compound with a paraffinic hydrocarbon results in WSD's lower than those found with either pure compound (reference 5). In addition, the effects of certain additives seem to depend on the composition of the base stock and test results are not always in agreement with those found using real fuels (reference 6). For these reasons, it was decided to use JP-5 fuel as the base fuel.

c. Initial tests with fuels from several different refineries and Naval Air Stations revealed that all of them had good lubricity. In order to make it easier to compare the effects of various additives and impurities on lubricity, it was decided to make the lubricity of the base fuel worse by filtering it through attapulgus clay. The clay filtration increased the WSD of the base fuels from less than 0.42 mm to greater than 0.50 mm. Differences in base line data found in different sections of this report are due to batch to batch variation in base fuels.

d. Base fuels were changed regularly to insure that test results were independent of fuel sources. Test fuels were drawn from fuel samples received from all over the continental United States. Test results obtained using a single base fuel were spot checked using other base fuels to eliminate any possible fuel effects.

e. In addition to using clay filtered JP-5, selected tests were run using unfiltered JP-5 and/or Ashland 140 solvent (a severely hydrotreated petroleum product manufactured by Ashland Chemical Company, Ashland, Kentucky, with properties similar to those of JP-5). The 140 solvent had very poor lubricity, normally giving WSD's of between 0.70 mm and 0.80 mm under standard operating conditions. Properties of a typical JP-5 and 140 solvent are listed in Appendix C.

5. Scuffing and Non-Scuffing Wear.

a. There are two types of wear that can occur with the BOCM: ordinary wear and scuffing wear. Scuffing wear is a catastrophic form of adhesive wear resulting from failure of the surface film. Scuffing is accompanied by the rubbing away of large, visible pieces of metallic debris.

b. In the BOCM, the occurrence of scuffing depends on the lubricity of the fuel and the severity of the test conditions. For example, isooctane will begin to scuff after about four minutes under standard operating conditions while 140 solvent will only scuff under conditions of high humidity and JP-5 will not scuff at all under the most severe conditions tried (1400 g load, 80 percent R.H.). WSD's obtained under scuffing conditions cannot be compared to non-scuffing data because the wear modes are different. The onset of scuffing is, however, a sign that the fluid being tested has very poor lubricity.

6. Effect of Impurities on Lubricity. The effects of trace levels of sulfur, nitrogen and oxygen compounds representative of those found in JP-5 were evaluated.

a. Sulfur Compounds. The maximum allowable concentration of sulfur in JP-5 is limited by MIL-T-5624K to 0.4 percent (wt) sulfur or about two percent (wt) sulfur compounds; however, typical JP-5 fuels usually contain less than 0.1 percent (wt) sulfur. Four sulfur compounds were evaluated at concentrations up to 2500 ppm (0.25 percent). Data is presented in Table II. None of the materials examined improved lubricity; one made lubricity considerably worse.

b. Nitrogen Compounds. MIL-T-5624K does not set an upper limit for the nitrogen concentration of JP-5; however, reference 7 reported the maximum expected concentration of nitrogen compounds in JP-5 to be about 1000 ppm. The effects of up to 500 ppm of nitrogen containing compounds on lubricity were measured. Data is presented in Table III. All of the materials tested, except one, significantly improved the lubricity of clay filtered JP-5 at concentrations below 500 ppm. Minimal additional effects were realized by increasing the nitrogen concentration beyond the level needed to get a WSD of approximately 0.27 mm.

c. Oxygen Compounds (other than organic acids). MIL-T-5624K does not specify an upper limit for the oxygen concentration of JP-5; however, reference 7 reported that JP-5 might contain as much as 1000 ppm of oxygen containing compounds. Five types of oxygen compounds were evaluated in clay filtered JP-5 at concentrations up to 500 ppm. Results are listed in Table IV. None of the compounds improved lubricity at low concentrations; three provided moderate improvement at high concentrations while two made lubricity worse.

d. Organic Acids.

(1) The maximum allowable acid number in JP-5 is limited by MIL-T-5624K to 0.015 $\frac{\text{mg KOH}}{\text{g fuel}}$ or about 46 ppm (wt) as decanoic acid. Organic

acids of all types (paraffinic, aromatic and naphthenie) were found to significantly improve the lubricity of JP-5 fuel at concentrations well below the maximum allowable. Data on a variety of acids is presented in Table V. The effectiveness of all acids increases very rapidly with increasing concentration until a WSD of about 0. mm is achieved. Further additions of acid have only minimal effects on lubricity.

(2) Correlation between acid number and WSD. Since organic acids were shown to improve the lubricity of JP-5, a study was made to determine whether the measured acid numbers (ASTM-D-3242) of fuels would correlate with their lubricity. Results are shown in Table VI. They indicate that WSD's tend to get smaller as acid number increases. The scatter of the data, however, appears to preclude using acid number to predict WSD. The lack of a strong correlation between acid number and WSD is probably due to the fact that impurities other than acids also contribute to lubricity.

e. Combinations of Elements. The effects of several compounds containing more than one heteroatom are shown in Table VII. Compounds containing only nitrogen and oxygen have positive effects on lubricity; none of the compounds containing sulfur had any positive effects on lubricity.

f. These results show that impurities play a significant role in determining the lubricity of JP-5 and that their removal by hydrotreating or filtration will result in a fuel with poor lubricity.

7. Effects of Additives on Lubricity. The additives evaluated in this report are those which were approved for use at the time the work was done. Changes since then have removed some of the anti-oxidants from the qualified products list.

a. Anti-icing Additive. The current anti-icing additive, ethylene glycol monomethyl ether, has no measureable effect on lubricity at concentrations up to the maximum allowed in JP-5 (0.15 percent volume).

b. Corrosion Inhibitors

(1) Corrosion inhibitors have been found to be effective lubricity improvers. They are required in JP-4 for lubricity reasons; however, they are not permitted in JP-5 without prior approval. One of the approved corrosion inhibitors, Hitec E-515, is currently being used in ships of the fleet as a lubricity improver.

(2) The effect of twelve additives listed in reference 8 on the lubricity of clay filtered JP-5 was determined. Each additive was evaluated at its relative effective, minimum effective and maximum allowable concentrations. Test results are shown in Table VIII. They show that all of the additives improved the lubricity of clay filtered JP-5 at all concentrations

tried. The effectiveness of each additive increased with increasing concentrations. These results are very similar to those reported in reference 3 on the effect of corrosion inhibitors on the lubricity of an aromatic-free solvent.

(3) The similarities between corrosion inhibitors and organic acids are not coincidental. Although their actual formulations are proprietary, several of the inhibitors are known to contain organic acids as one of their active ingredients.

c. Anti-oxidants. The effect of anti-oxidants approved for use in JP-5 was determined. Two general types of anti-oxidants were evaluated: phenols and phenylene diamines. The compounds tested were evaluated at their maximum allowable concentrations in JP-5. Test results, presented in Table IX, show that none of the anti-oxidants evaluated had any significant effects on lubricity.

d. Other Additives. The effectiveness of a lubricity additive used in JP-7 (MIL-T-38219), PWA-536, was evaluated. PWA-536 is required in JP-7 at a concentration of between 200 and 300 ppm (vol). Test results are shown in Figure 3. They show that the effectiveness of PWA-536 is a linear function of its concentration in 140 solvent. In addition, it requires a much higher concentration than the corrosion inhibitors to be equally effective.

8. Effect of Pure Compounds. The effects on lubricity of pure compounds representative of those typically found in JP-5 were evaluated. The types of compounds studied were straight and branched chain paraffins, aromatics and polycyclic aromatics. Up to five percent (vol) of each compound was added to clay-filtered JP-5. The pure materials were filtered through silica gel and 0.22 micron millipore filters to remove impurities before being added to the test fuel. Test results, listed in Table X, show that moderate changes in composition do not significantly improve the lubricity of JP-5. In some cases, the lubricity of the fuel with added pure material is worse than the original.

9. Effects of Fuel Composition. The effects of changes in fuel composition on lubricity were evaluated using a series of JP-5 fuels that were blended at a refinery as part of a study on the effects of broadening fuel specifications on performance (reference 9). The specification changes evaluated were distillation end point, olefin content, aromatic content and naphthalene content. Each fuel was clay-filtered before testing to remove any impurities that might interfere with results. Test results, including detailed specification changes for each fuel, are presented in Table XI. They show that large increases in distillation end point, naphthalene content, aromatics content and olefins content will lower the WSD of JP-5 fuel; however, the size of the decreases effectively precludes specification changes from being a practical method of lowering WSD.

10. Effect of Blending Fuels on Lubricity.

a. Under field conditions, it would be rare that a single batch of

fuel would go from refinery to aircraft without being mixed with other batches of fuel. For this reason a study was made to determine the effects of blending fuels with different lubricities on WSD. The fuels tested were JP-5, clay-filtered JP-5, and 140 solvent. Each fuel was blended with the others in varying proportions and the WSD's of the blends measured. Results are presented in Figure 4. They show that blending small amounts of JP-5 with either clay-filtered JP-5 or 140 solvent results in a large decrease in WSD while blending clay-filtered JP-5 with 140 solvent results in a roughly linear graph of concentration versus WSD over the entire concentration range.

b. These results can be explained by referring back to the work done on the effects of impurities on lubricity. That work showed the WSD decreased rapidly with increasing impurity concentration until a certain threshold concentration was reached. Beyond this threshold concentration, further additions of impurity had very little effect on WSD (Tables III, IV, V and VII).

c. In Figure 5, the type of response shown for individual impurities is generalized to the case of a real fuel, which will contain many different types of impurities. The actual impurity concentrations are not shown because they would vary depending on the specific impurities present.

d. For a fuel with good lubricity, there is a good chance that its impurity level will fall on the flat portion of Figure 5 (Point A); i.e., there is an "excess" of impurity over the amount needed to achieve the good lubricity. When a small amount of a good lubricity fuel with an excess of impurity is mixed with a fuel with little (clay-filtered, Point B) or no (140 solvent, Point C) impurity, the total impurity level is shifted to the vicinity of Point D. Due to the steepness of the curve in the low concentration range, the small increase in impurity level causes a large decrease in WSD.

e. If two fuels with little or no impurities are mixed (Points B and C), there is no "excess" impurity available and the lubricity of the mixture varies with the concentration of the individual components in an approximately linear relationship.

f. The technique of blending small amounts of a fuel having good lubricity with a fuel with poor lubricity to bring the lubricity of the blended fuel into the acceptable range could be utilized in the field to help prevent problems caused by poor lubricity fuel. For example, if a batch of fuel known to have been severely hydrotreated is received, it could be split up among a large number of storage tanks, each of which already contains some fuel having good lubricity, instead of being stored separately in one or two tanks.

11. Effect of Large Changes in Humidity on Lubricity. The effects of large changes in humidity on WSD are shown in Figure 6. Three fluids were studied: JP-5, clay-filtered JP-5 and 140 solvent. Each fuel reacted differently to changes in humidity. The WSD of the JP-5 increased

slowly with increasing humidity until the relative humidity reached 40 percent. Further increases in humidity had no effect on WSD. The WSD of the clay-filtered JP-5 increased slowly with increasing relative humidity over the entire range of humidities tested. The WSD of the 140 solvent increased rapidly with increasing humidity between 0 and 30 percent R.H. Above 30 percent R.H. scuffing occurred and made accurate measurements of WSD impossible.

12. Effect of Dissolved Oxygen on Lubricity.

a. The effect of dissolved oxygen on lubricity was determined. Three test fluids were used: JP-5, clay-filtered JP-5, and 140 solvent. Oxygen was removed from the system by purging the test fluid with nitrogen instead of air. The oxygen content of the test fluid was not measured.

b. It was found that removing oxygen lowered the WSD's of the clay-filtered JP-5 and the 140 solvent from over 0.60 mm to less than 0.30 mm while it had only a small effect on the WSD of JP-5. Test results are shown in Table XII. They show that even under the most severe conditions (80 percent R.H.), the WSD of 140 solvent and clay-filtered JP-5 remained very low. In addition, the use of high concentrations of two lubricity improving materials, Hitec E-515 and dilinoleic acid, had no additional effect on the lubricity of the deoxygenated 140 solvent or clay-filtered JP-5.

c. The significant increases in wear caused by oxygen have previously been reported in reference 10. Reference 10 attributed the increase in wear in the presence of oxygen to a simple corrosive wear mechanism, involving the formation and rubbing away of metal oxides on the metal surface.

d. In order to understand why oxygen had only a small effect on the lubricity of unfiltered JP-5 and why known lubricity improvers had no effects on deoxygenated fuel, it is necessary to examine what is occurring at the metal-test fluid interface. At the interface, dissolved oxygen competes with polar materials in the test fluid for adsorption on the metal surface. When both are present, the polar materials are preferentially adsorbed and prevent the oxygen from reaching the surface and reacting there. This is why unfiltered JP-5 and fluids having a sufficient concentration of added polar materials have good lubricity. They have a relatively high concentration of polar materials which adsorb on the surface and keep most of the oxygen away. Thus the removal of the dissolved oxygen by nitrogen purging has little effect. Clay-filtered JP-5 and 140 solvent, on the other hand, contain very few polar compounds. Hence, more oxygen can reach the surface and react to form oxides which are worn away at high rates. Removal of oxygen by nitrogen purging significantly lowers the oxygen concentration on the surface and hence significantly lowers the wear rate also.

e. An examination of the data in Tables III, V, VIII, and XII indicates that preventing oxygen from reaching the surface by nitrogen sparging or by the addition of polar materials such as organic acids, corrosion inhibitors

and nitrogen containing compounds will only lower the WSD of JP-5 fuel or 140 solvent to about 0.27 mm under standard operating conditions. Once WSD is achieved, further additions of polar compounds have virtually no effect on WSD. This is also illustrated in Table XIII, which shows the effects of very high concentrations of Hitec E-515 on the WSD of 140 solvent. The data shows that once a WSD of about 0.27 mm is reached, further additions of Hitec E-515 have very little effect.

f. Thus it appears that wear phenomena observed in the BOCM using JP-5 and 140 solvent can be divided into two types: oxygen-related wear and non-oxygen related wear. Under standard conditions, WSD's above 0.27 mm can be attributed to oxygen reaching the surface, reacting and the reaction products being worn away. Non-oxygen related wear, which is believed to be dependent on the physical properties of the test fluid, produces a fixed WSD of about 0.27 mm under standard conditions for JP-5 and similar fluids.

13. <u>Effect of Large Load Changes on Lubricity.</u> The effect of large changes in load on the lubricity of three test fluids, JP-5, clay-filtered JP-5, and 140 solvent, was examined. Data is presented in Table XIV. JP-5 fuel acts about as expected; its WSD increases steadily from 0.20 mm to 0.31 mm as the applied load is raised from 200 g to 1200 g. Clay-filtered JP-5 and 140 solvent act differently. Their WSD's go through a maximum at a low load, then show a rapid decrease followed by a slow increase at highest loads. This unusual behavior is believed to be related to the lack of polar impurities in the two fuels. At low loads, oxygen is able to react on the surface to form corrosion products that are rapidly worn away. As the load is increased, the temperature at the point of contact between the ball and cylinder increases rapidly. (According to reference 11, local surface temperature increases as (load) $^{1/4}$. Thus if the load is tripled, local temperature, in degrees centigrade, increases by a factor of about 1.3). The high local temperatures can cause the thermal and oxidative breakdown of normally non-reactive components in the test fluid to produce reactive components. These reactive components may then be adsorbed on the surface and keep some of the oxygen away. This results in lower WSD's. As loads increase further, the effect of the higher load begins to overcome the effects of the newly formed reactive materials and WSD's begin to increase again.

14. The results of the work on large changes in load, humidity, and oxygen content indicate that extreme caution should be taken when comparing WSD's obtained under different operating conditions. In addition, comparing two fluids based on data obtained at other than standard conditions should be avoided because differences between fuels may be increased or decreased by changing conditions. Data from non-standard operating conditions should be used only if a series of known reference fluids has been evaluated under the same conditions.

FIGURE 1: SCHEMATIC OF BALL-ON-CYLINDER MACHINE

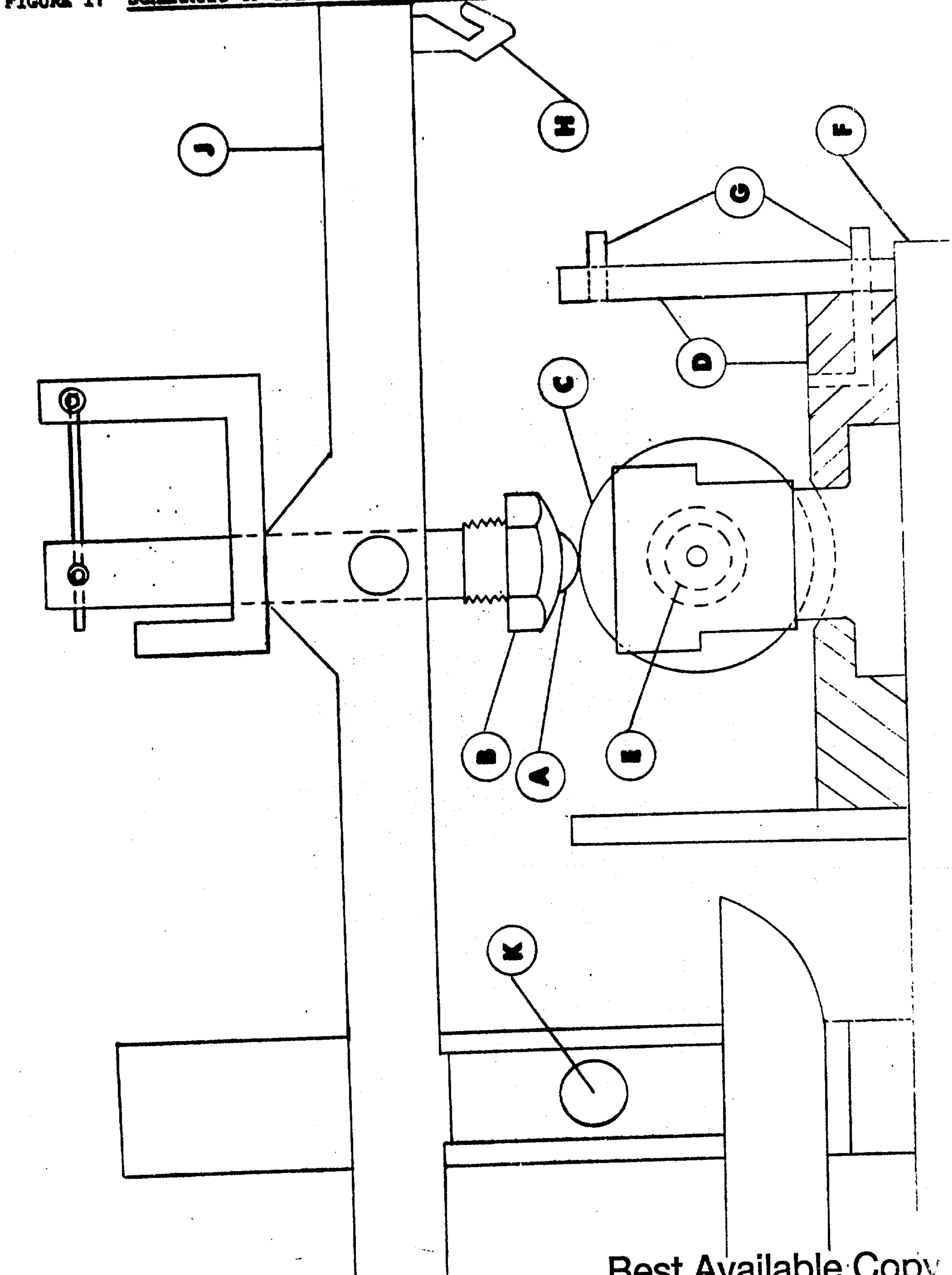

FIGURE 2: PHOTOGRAPH OF BALL-ON-CYLINDER MACHINE

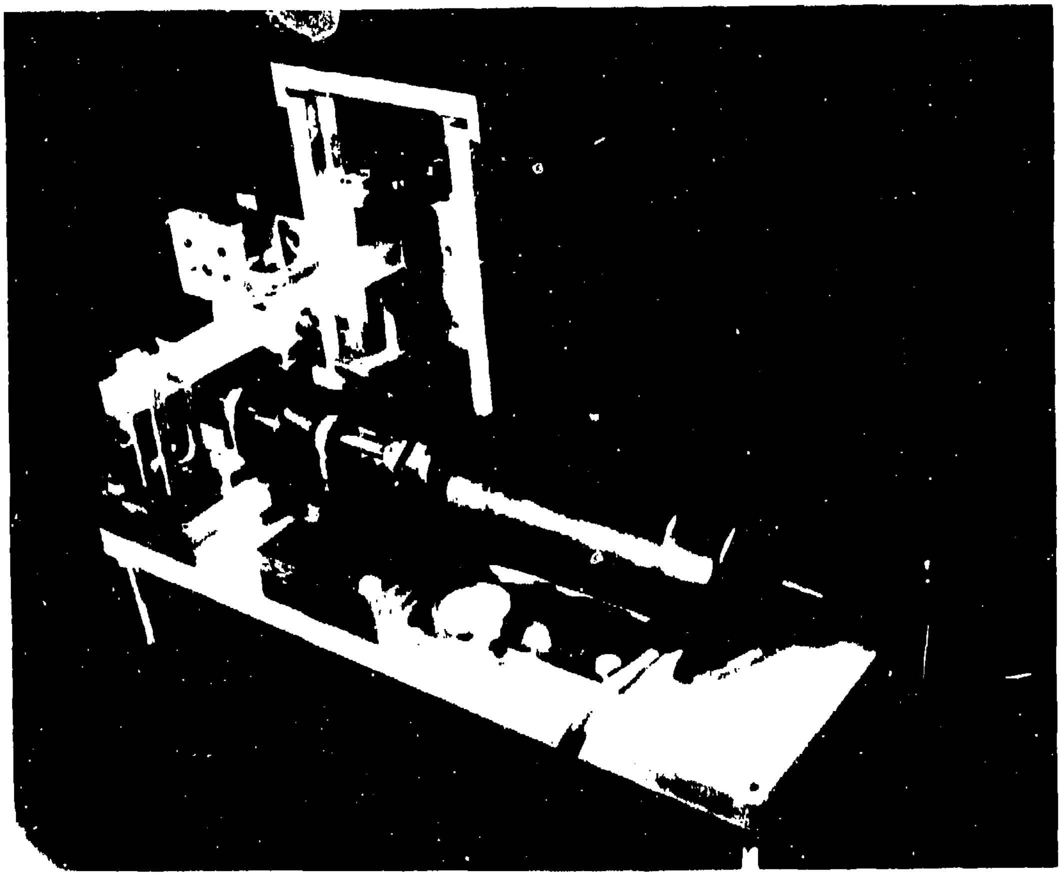

FIGURE 3: EFFECT OF PWA 536 ON LUBRICITY OF 140 SOLVENT

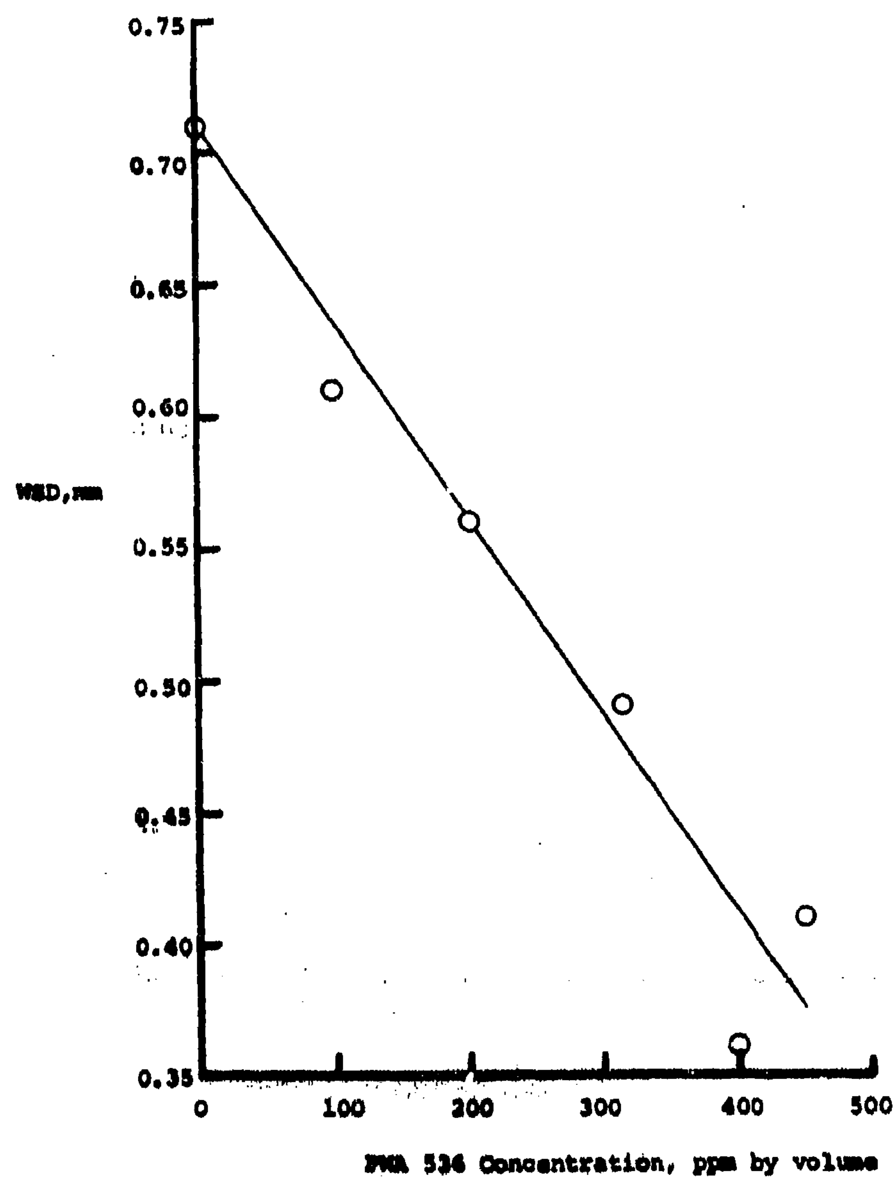

FIGURE 4: EFFECT OF BLENDING FUELS ON LUBRICITY

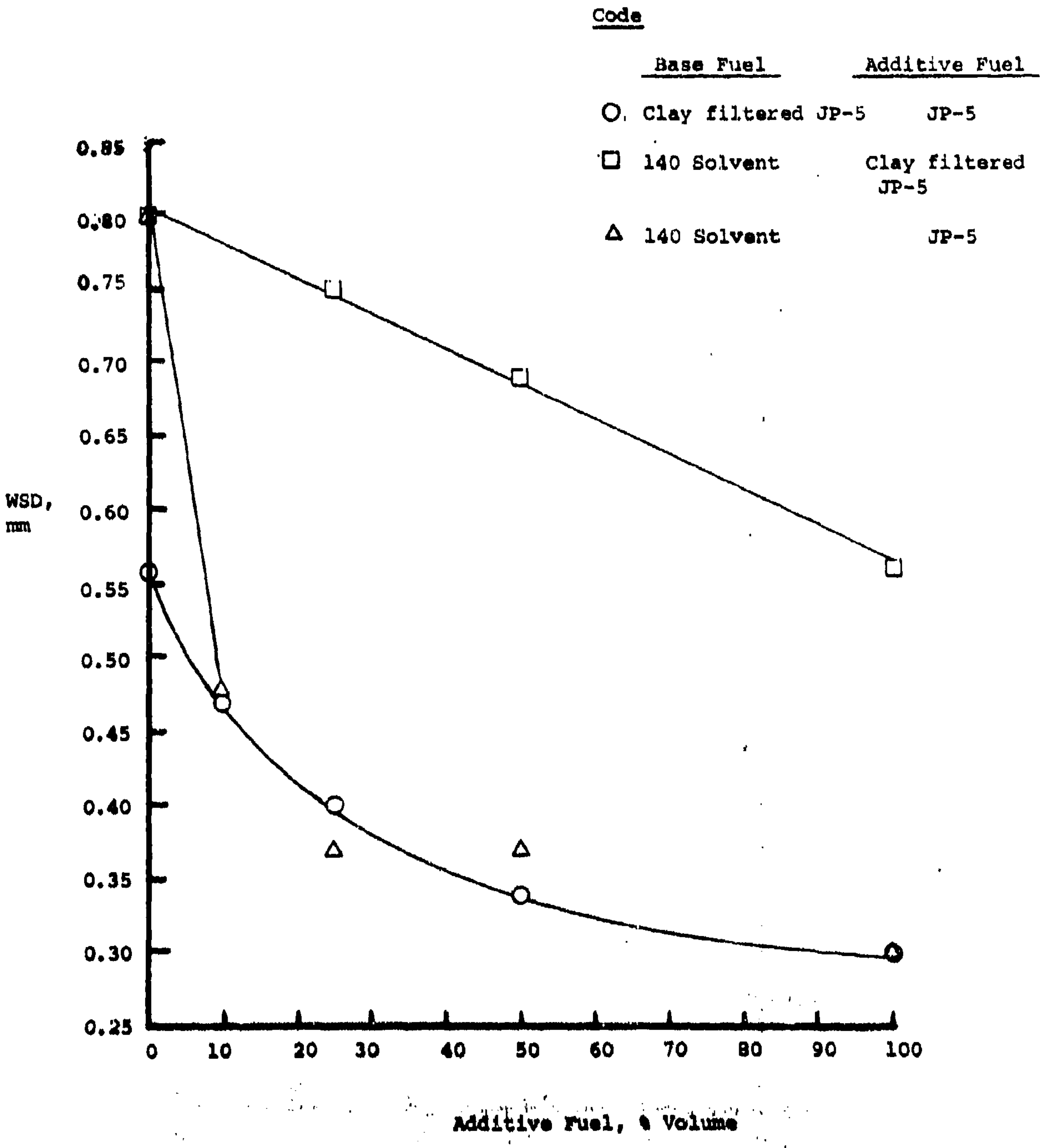

FIGURE 5: IDEALIZED EFFECT OF IMPURITY CONCENTRATION ON LUBRICITY

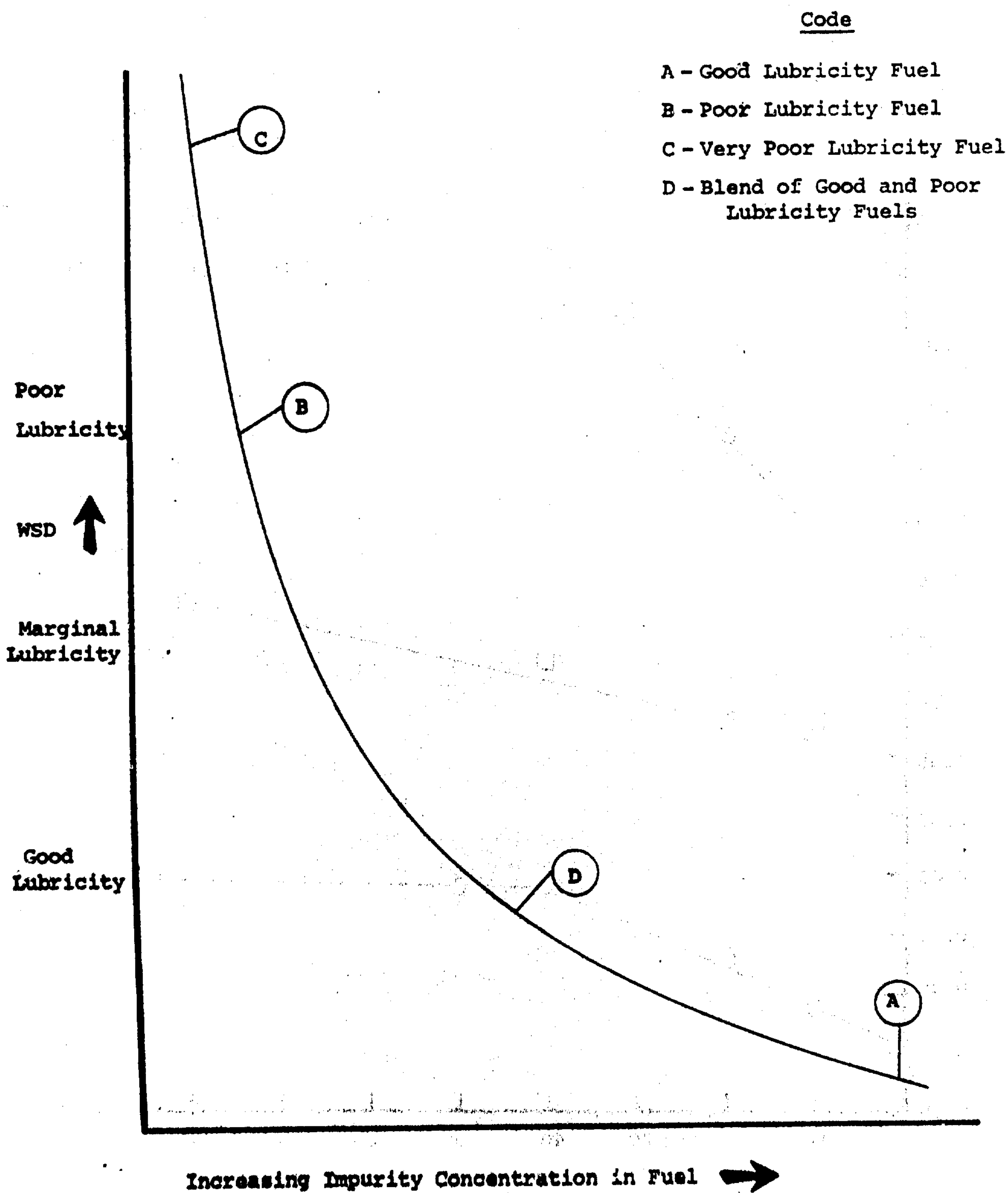

FIGURE 6: EFFECT OF HUMIDITY ON WEAR SCAR DIAMETER

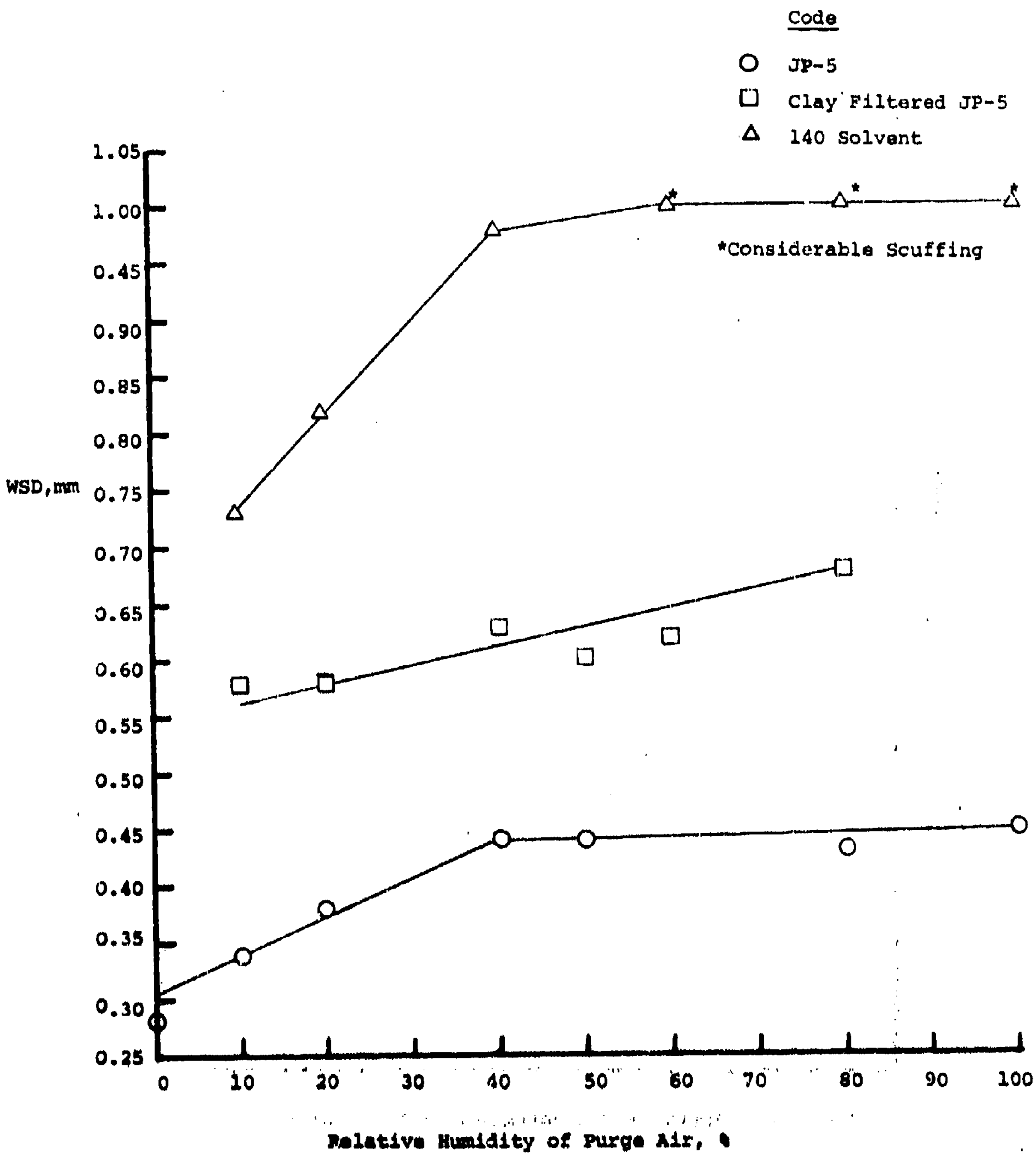

TABLE I

EFFECT OF SMALL CHANGES IN RPM, LOAD AND TEST DURATION ON WEAR SCAR DIAMETER

RPM	Load, (g)	Test Duration, min.	WSD, mm
230	1,000	32	0.60
240	1,000	32	0.60
250	1,000	32	0.60
240	940	32	0.57
240	1,000	32	0.60
240	1,040	32	0.60
240	1,000	28	0.63
240	1,000	32	0.65
240	1,000	36	0.67

NOTE: Clay filtered JP-5 used for all tests.

TABLE II

EFFECT OF SULFUR COMPOUNDS ON LUBRICITY

Name	Type	Concentration, ppm	WSD, mm
Base Fuel (clay filtered JP-5)	-	-	0.57
Butyl disulfide	disulfide	20 (vol)	0.63
		100 (vol)	0.60
		2,500 (vol)	0.65
Thioxanthene	aromatic	200 (vol)	0.55
		2,500 (vol)	0.59
α-toluenethiol	thiol	20 (vol)	0.77
		100 (vol)	0.80
		2,500 (vol)	1.01
Dibenzothiophene	thiophene	2,500 (wt)	0.55

TABLE III

EFFECT OF NITROGEN COMPOUNDS ON LUBRICITY

Name	Type	Concentration, ppm	WSD, mm
Base Fuel (clay filtered JP-5)	-	-	0.57
N-methyl anoline	aromatic amine	100 (vol)	0.57
		500 (vol)	0.53
N-ethyl diethanol amine	non-aromatic amine	20 (vol)	0.33
		100 (vol)	0.28
		500 (vol)	0.26
2-methyl piperidine	non-aromatic heterocyclic	20 (vol)	0.55
		100 (vol)	0.50
		500 (vol)	0.36
Octadecylamine	paraffinic amine	20 (wt)	0.43
		200 (wt)	0.27
		500 (wt)	0.27
Bathophenanthroline	pyridine	20 (wt)	0.50
		200 (wt)	0.35

TABLE IV

EFFECT OF NON-ACIDIC OXYGEN COMPOUNDS ON LUBRICITY

Name	Type	Concentration, ppm	WSD, mm
Base Fuel (clay filtered JP-5)	-	-	0.57
Methyl octonoate	ester	100 (vol)	0.64
		500 (vol)	0.87
5,5 dimethyl-1,3 cyclohexanedione	ketone	20 (wt)	0.66
		100 (wt)	0.40
		200 (wt)	0.35
		500 (wt)	0.39
4-test-butyl-2-methyl phenol	phenolic	100 (vol)	0.54
		500 (vol)	0.45
Diisopropyl benzene hydroperoxide	hydroperoxide	100 (vol)	0.68
		500 (vol)	0.51
Dibenzofuron	furan	500 (wt)	0.83
Copper acetylacetonate	-	20 (wt)	0.61
		100 (wt)	0.54
		200 (wt)	0.40

TABLE V

EFFECT OF ORGANIC ACIDS ON LUBRICITY

Acid	Concentration, ppm	WSD, mm
None (clay filtered JP-5)	-	0.56
Palmitic	2.1 (wt)	0.54
	3.2 (wt)	0.46
	4.3 (wt)	0.38
	10.8 (wt)	0.32
Stearic	2.0 (wt)	0.55
	3.0 (wt)	0.82
	4.1 (wt)	0.44
	10.4 (wt)	0.32
Lauric	1.8 (wt)	0.56
	2.7 (wt)	0.52
	3.4 (wt)	0.48
	3.6 (wt)	0.42
	11.0 (wt)	0.32
Decanoic	1.3 (wt)	0.53
	1.8 (wt)	0.50
	3.6 (wt)	0.40
	10.8 (wt)	0.30
Oleic	1.6 (vol)	0.57
	2.4 (vol)	0.52
	3.2 (vol)	0.35
	4.8 (vol)	0.36
	10.0 (vol)	0.31

TABLE V (Continued)

Acid	Concentration, ppm	WSD, mm
Dilinoleic	3.2 (vol)	0.58
	4.0 (vol)	0.52
	4.8 (vol)	0.48
	6.4 (vol)	0.37
	10.0 (vol)	0.30
Linoleic	7.5 (vol)	0.31
	15 (vol)	0.30
	30 (vol)	0.28
Ethyl hexanoic	7.5 (vol)	0.40
	15 (vol)	0.38
	30 (vol)	0.35
Naphthenic	5 (vol)	0.52
	10 (vol)	0.36
	20 (vol)	0.30
	30 (vol)	0.30

TABLE VI

EFFECT OF MEASURED ACID NUMBER ON LUBRICITY

Fuel	Acid Number, mg KOH*/g fuel	WSD, mm
Clay Filtered JP-5	0.00005	0.56
Harpoon Fuel	0.00057	0.57
JP-5	0.00059	0.49
Jet A	0.00063	0.40
JP-5	0.00077	0.40
JP-4	0.00077	0.52
JP-5	0.00083	0.48
JP-5	0.00091	0.25
JP-5	0.00127	0.33
JP-5	0.0063	0.39

*Measured according to ASTM-D-3242.

TABLE VII

EFFECTS OF COMPOUNDS CONTAINING MORE THAN ONE TYPE OF HETERO ATOM ON LUBRICITY

Name	Hetero-atoms	Concentration, ppm	WSD, mm
Base Fuel (clay filtered JP-5)	-	-	0.57
Nitroso-betanaphthol	N,O	20 (wt)	0.39
		200 (wt)	0.26
p-nitrophenol	N,O	20 (wt)	0.41
		200 (wt)	0.31
Sulfanilamide	N, O, S	200 (wt)	0.57
Diphenylthiocarbazone	N, S	200 (wt)	0.74
Diethyldithiocarbamic acid, sodium salt	O, S	200 (wt)	0.66
p-tolyl sulfoxide	O, S	200 (wt)	0.59

TABLE VIII

EFFECT OF CORROSION INHIBITORS ON LUBRICITY

Relative Effective Concentration*			Minimum Effective Concentration*			Maximum Allowable Concentration*		
Additive	Conc. lb/1000 bbl	WSD, mm	Additive	Conc. lb/1000 bbl	WSD, mm	Additive	Conc. lb/1000 bbl	WSD, mm
None (clay filtered JP-5)	-	0.61	None	-	0.61	None	-	0.61
PRI-19	2	0.60	PRI-19	3	0.56	Lubrizol 541	6	0.40
Tolad 245	5	0.58	NALCO 5403	3	0.53	Tolad 245	12	0.36
Nalco 5403	2	0.58	Hitec E580	3	0.51	Unicor J	8	0.35
Nalco 5402	2	0.58	Nalco 5402	3	0.50	PRI-19	8	0.33
Hitec E580	2	0.57	Tolad 246	3	0.49	Nalco 5403	8	0.31
Tolad 246	2	0.54	Lubrizol 541	3	0.48	Nalco 5402	8	0.31
DCI-6A	2	0.52	DCI-4A	3	0.45	Tolad 246	8	0.31
Lubrizol 541	2	0.52	Tolad 245	7.5	0.44	DCI-6A	8	0.31
DCI-4A	2	0.50	DCI-6A	3	0.40	Hitec E580	8	0.30
Emery 9855	3	0.48	Unicor J	3	0.40	DCI-4A	8	0.29
Unicor J	2	0.43	Emery 9855	4.5	0.38	Emery 9855	12	0.29
Hitec E515	5	0.43	Hitec E515	7.5	0.35	Hitec E515	16	0.29

*Obtained from reference 8

TABLE IX

EFFECT OF ANTI-OXIDANTS ON LUBRICITY

Anti-Oxidant	Concentration of Active Ingredients	WSD (mm)
None (clay filtered JP-5)	-	0.65
Phenylenediamines		
N, N' disecondary-butyl-paraphenylenediamine	30 ppm (vol)	0.56
N, N' di-isopropyl paraphenylenediamine	30 ppm (vol)	0.60
Phenols		
100% alkylated phenols, principally 2, 4 ditertiary butylphenol	30 ppm (vol)	0.56
100% alkylated phenols, principally 2, 4 dimethyl 6-tertiary butylphenol (min 72%)	30 ppm (vol)	0.65
55% min. 6- tert-butyl-2, 4-dimethylphenol 45% max. mixture of tert-butylphenols and di-tert-butylphenols	30 ppm (vol)	0.61
2, 6 ditertiarybutyl 4-methylphenol	30 ppm (wt)	0.63

TABLE X

EFFECT OF PURE COMPOUNDS ON LUBRICITY

Compound	WSD (mm)
Base fuel (clay filtered JP-5)	0.60
2% (vol) n-dodecane	0.73
5% (vol) n-dodecane	0.65
2% (vol) 1-methyl naphthalene	0.57
5% (vol) 1-methyl naphthalene	0.73
2% (vol) butyl benzene	0.51
5% (vol) butyl benzene	0.56
5% (vol) 2,2,5 - trimethyl hexane	0.57

TABLE XI

EFFECT OF CHANGES IN FUEL COMPOSITION ON WEAR SCAR DIAMETER

Fuel Number	1	2	3	4	5	6
Distillation End Point, °F	490	580	514	513	514	510
Aromatics, %	10.6	13.7	24.9	40.0	24.9	26.1
Olefins, %	0.8	1.1	1.9	1.9	1.9	8.4
Fuel Composition Changes	JP-5 base fuel	Aromatic compounds typical of those found in JP-5 added to base fuel	Naphthalenes increased to 4% and other aromatics added to base fuel	Aromatic compounds typical of those found in JP-5 added to base fuel	Dicyclic polynuclear aromatics added to base fuel	Aromatics and olefins typical of those found in JP-5 added to base fuel
WSD, mm	0.67	0.62	0.51	0.48	0.47	0.46

TABLE XII

EFFECT OF DISSOLVED OXYGEN ON LUBRICITY

Fuel	Atmosphere	Test Conditions*	Additives	WSD, mm
JP-5	Air	-	-	0.30
	N_2	-	-	0.24
Clay filtered JP-5	Air	-	-	0.61
	N_2	-	-	0.22
	N_2	-	7.5 ppm (vol) dilinoleic acid	0.24
140 Solvent	Air	-	-	0.80
	Air	80% relative humidity	-	1.00(scuffing)
	N_2	-	-	0.27
	N_2	80% relative humidity	-	0.27
	N_2	600 g load	-	0.22
	N_2	-	50 ppm (vol) Hitec E515	0.25

*Variations from standard operating conditions

TABLE XIII

EFFECT OF HIGH CONCENTRATIONS OF HITEC E515

ON THE LUBRICITY OF 140 SOLVENT

Additive Concentration, ppm (vol)	WSD, mm
None (140 solvent)	0.69
12.5	0.42
25	0.31
50	0.30
100	0.27
200	0.25

TABLE XIV

EFFECT OF LARGE LOAD CHANGES ON LUBRICITY

	WSD, mm		
Load	JP-5	Clay filtered JP-5	140 Solvent
200	0.20	0.68	0.81
400	0.24	0.75	0.85
600	0.25	0.86	0.80
800	0.29	0.62	0.66
1000	0.30	0.60	0.76
1200	0.31	0.64	0.75
1400	-	-	0.85

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9. PRIVATE COMMUNICATION - U.S. Army Fuels and Lubricants Research Laboratory, San Antonio, Texas

10. ARTICLE - Appeldoorn, J. K., Goldman, I. B. and Tao, F. F., "Corrosive Wear by Atmospheric Oxygen and Moisture," ASLE Transactions, 12, 140-150 (1969)

11. REPORT - Klaus, E. E. et al "Fluids, Lubrication, Fuels and Related Materials," Pennsylvania State University (prepared for Air Force Materials Laboratory) June 1974

APPENDIX A

SPECIFICATIONS FOR BALLS AND CYLINDERS

Balls

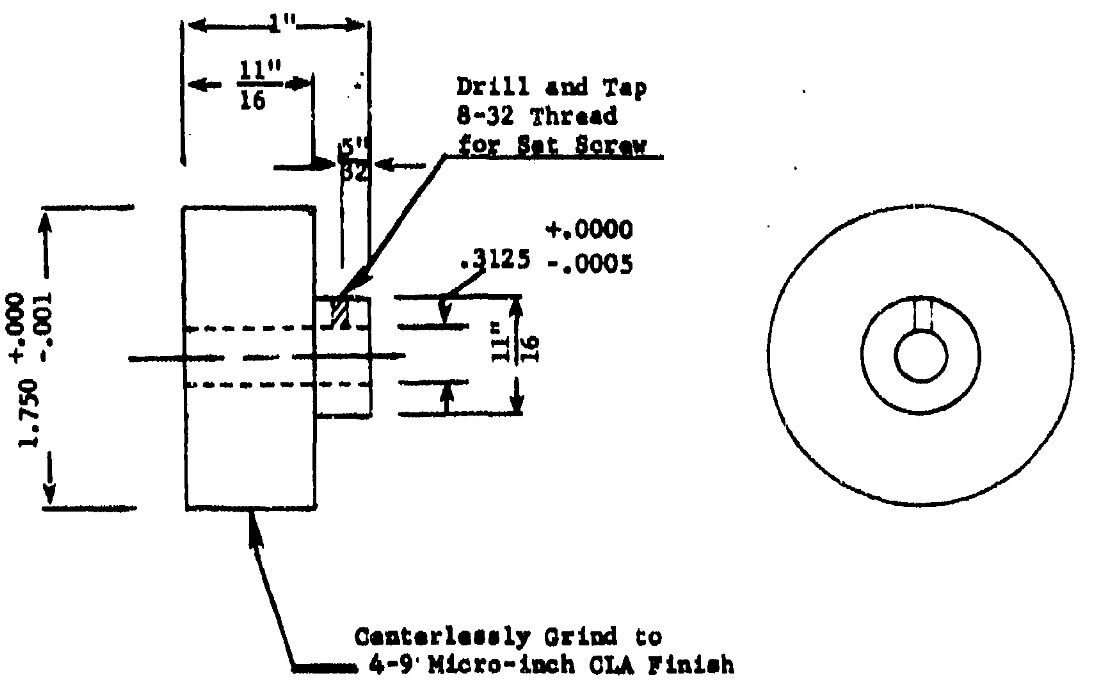
Material: AISI 52100 Steel

Hardness: 62-64 Rockwell C

Source: Grade 25 EP manufactured by SKF for the Shell four ball tester (ASTM D-2596)

Cylinders: Specifications shown on next page.

CYLINDER FOR BALL-ON-CYLINDER MACHINE



NOTES:

1. Material: AISI 52100 Steel
2. Hardness: Quench and Temper to 20-22 Rockwell C

APPENDIX B

CLEANING PROCEDURE FOR BALL-ON-CYLINDER MACHINE

A. Cylinders - Initial Clean-up

1. Wash with lab detergent and water. Use soft bristled brush. Avoid scratching polished surface with a metal brush handle.

2. Rinse thoroughly with distilled water.

3. Air dry.

4. Clean in Soxhlet extractor using a 50/50 mixture of isopropyl alcohol and toluene or xylene. Reflux for 15 cycles or two hours, whichever is greater.

5. Dry in vacuum desiccator for 8 hours.

6. Store in desiccator.

B. Balls

1. Rinse with solvent to remove bulk of oil coating.

2. Follow Steps 4-6 in A.

C. Reservoir

1. Disassemble reservoir for cleaning after each run.

2. Clean reservoir with isooctane.

3. Dry with vacuum.

D. Cylinder on Spindle (between runs)

1. Remove as much test fluid as possible from cylinder using suction and by wiping with tissue.

2. Rinse with osooctane.

3. Wipe with clean tissue or cloth.

4. Rinse and wipe again.

5. Dry with suction.

6. Make sure all fluid is removed from areas around set screw and shaft/cylinder contact areas.

APPENDIX C

CHEMICAL AND PHYSICAL PROPERTIES OF FUELS

Property	JP-5	140 Solvent
Distillation temperature, °C		
Initial boiling point	175	187
10 percent recovered	195.5	189
20 percent recovered	201	190
50 percent recovered	214	192
90 percent recovered	238	196.5
End point	256	211
Residue, vol. percent	1.2	1.0
Loss, vol. percent	0.0	1.0
Gravity, °API (sp. gr.)	42.8 (0.8118)	47.5 (0.7905)
Flash point, °C	66.5	64.5
Freezing point, °C	-49.0	-50.0
Viscosity, centistokes @ -20°C	5.7	4.0
Heating Value		
Aniline - gravity product	6,069	7,268
Net heat of combustion $(\frac{BTU}{lb})$	18,555	18,749
Smoke point, mm	22	33.0
Aromatics, vol. percent	20.97	7.4
Olefins, vol. percent	1.6	1.5
Sulfur, total weight percent	0.006	0.01
Copper strip corrosion, 2 hr. @ 100°C	1b	1b
Thermal stability		
Change in pressure drop, mm Hg	0.1	0.1
Preheater deposit code	1	1
Existent gum, mg/100 ml	4.0	1.2
Water separation index, modified	92	100
Total acid number, mg KOH/g	0.005	0.006

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